

# Initial-Stage Growth Controlled Crystal Orientations in Nanoconfined Lamellae of a Self-Assembled Crystalline-Amorphous Diblock Copolymer

L Zhu, BH Calhoun, Q Ge, RP Quirk, SZD Cheng (U. Akron), EL Thomas (M.I.T.), B.S. Hsiao, F Yeh, L Liu (SUNY, Stony Brook), B Lotz (Institute Charles Sadron, France)

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Beamline(s): X27C

**Introduction:** Polymers in confined environments are of great scientific interest. One convenient and effective way to construct well-defined and uniformly oriented nano-environments is to use diblock copolymers as templates. For example, confined polymer crystallization can be studied using microphase-separated crystalline-amorphous diblock copolymers.<sup>1</sup> To ensure a solid confinement environment, the amorphous blocks need to possess a glass transition temperature ( $T_g^a$ ) which is higher than the melting temperature of the crystals ( $T_m^c$ ) formed by the crystallizable blocks, namely,  $T_{ODT} > T_g^a > T_m^c$ .<sup>2</sup> Crystallization temperature ( $T_c$ )-dependant crystal orientations within nano-confined lamellae have been studied in a self-assembled poly(ethylene oxide)-*block*-polystyrene (PEO-*b*-PS) diblock copolymer. The copolymer forms a microphase separated lamellar structure in the melt. It has been found that the crystal (the *c*-axis) orientations of the PEO crystals are determined by only varying the  $T_c$ .<sup>3</sup>

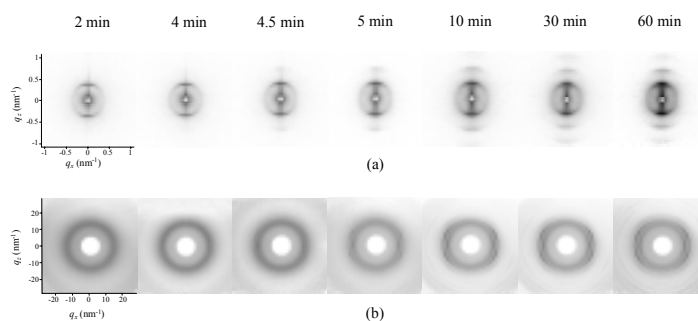
**Methods and Materials:** The PEO-*b*-PS diblock copolymer was synthesized via sequential anionic block copolymerization of styrene and ethylene oxide. It possesses number average molecular weights of  $\overline{M}_n^{\text{PEO}} = 8.7\text{k}$  and  $\overline{M}_n^{\text{PS}} = 9.2\text{k}$ , and the polydispersity of 1.04 in the final diblock copolymer was determined by SEC using a universal calibration. Simultaneous two-dimensional (2D) SAXS and WAXS experiments were carried out at the synchrotron X-ray Beamline X27C at the National Synchrotron Light Source in Brookhaven National Laboratory. The wavelength of the X-ray beam was 0.1307 nm. Isothermal crystallization measurements were carried out on a customized two-chamber hot stage. The samples were preheated to 70 °C in the melting chamber for 3 min, and then quenched (switched) to the second chamber with preset temperatures for isothermal crystallization.

**Results:** Based on real-time simultaneous two-dimensional (2D) small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) experiments (see Figure 1), the oriented PEO crystal diffractions are found at 4-4.5 min during isothermal crystallization at 36°C. At this early crystallization time, the PEO crystallinity is estimated to be around 4wt%. This result indicates that the formation of crystal orientation is in an early stage of PEO crystallization confined between the PS layers. In order to understand whether the crystal orientation is determined during the primary nucleation or crystal growth step, specifically designed self-seeded crystallizations are studied using 2D SAXS and WAXS techniques. Experimental results suggest that primary nuclei (self-seeds) do not possess specific orientation with respect to the PS lamellar surface normal, disregarding the history of crystal orientation in the samples generated before the self-seeding process. It is found that the initial stage of crystal growth determines the final crystal orientation in the nano-confined lamellae. Studies of the correlation lengths (apparent crystallite sizes) along both [120] directions of the PEO crystals with various crystal orientations indicate that the PEO crystals formed in nano-confined lamellae undergo a change from a one-dimensional to a two-dimensional growth with increasing the  $T_c$ .

**Conclusions:** The crystal (the *c*-axis) orientation changes in a shear-aligned PEO-*b*-PS diblock copolymer within a nano-confined lamellar environment have been found to be dependent only upon the  $T_c$ . Using time-resolved simultaneous 2D SAXS and WAXS experiments, the crystal orientation is determined to occur in the early stage of crystallization.

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**References:** <sup>1</sup>Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Lotz, B. *Polymer* in press. <sup>2</sup>Zhu, L.; Chen, Y.; Zhang, A.; Calhoun, B. H.; Chun, M.; Quirk, R. P.; Cheng, S. Z. D.; Hsiao, B. S.; Yeh, F.; Hashimoto, T. *Phys. Rev. B*. **1999**, 60, 10022. <sup>3</sup>Zhu, L.; Cheng, S. Z. D.; Calhoun, B. H.; Ge, Q.; Quirk, R. P.; Thomas, E. L.; Hsiao, B. S.; Yeh, F.; Lotz, B. *J. Am. Chem. Soc.* **2000**, 122, 5957.



**Figure 1.** Sets of WAXS (a) and SAXS (b) patterns for the shear-aligned PEO-*b*-PS isothermally crystallized at 36 °C for different times. The SAXS intensity is in a logarithmic scale.